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A coprecipitation technique to prepare $Sr_{0.5}Ba_{0.5}Nb_2O_6$

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Abstract. An aqueous mixture of ammonium oxalate and ammonium hydroxide was used to coprecipitate barium and strontium ions as oxalates and niobium ions as hydroxide under basic conditions. This precursor on calcining at 750°C yielded $Sr_{0.5}Ba_{0.5}Nb_2O_6$ phase. This is a much lower temperature than that prepared by traditional solid state method (1000°C) as reported for the formation of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN). Transmission electron microscopic (TEM) investigations revealed that the average particle size was 80 nm for the calcined powders. The room temperature dielectric constant at 1 kHz was found to be 1100. The ferroelectric hysteresis loop parameters of these samples were also studied.

Keywords. Ceramics; oxides; electron microscopy; X-ray diffraction; ferroelectricity.

1. Introduction

Alkali niobates and tantalates ($LiNbO_3$ and $LiTaO_3$) (Navale *et al* 2005a, b) and alkaline earth niobates ($Sr_xBa_{1-x}Nb_2O_6$ ($0{\cdot}25 < x < 0{\cdot}75$)) are ferroelectric materials which have excellent electro-optic, pyroelectric and photo-refractive applications (Gaikwad *et al* 2004; Dhage *et al* 2005; Natarajan *et al* 2005; Pasricha and Ravi 2005; Ravi 2005). Although single crystals of varying chemical compositions of SBN find applications, there are still restrictions because of high cost and difficult fabrication. In contrast, polycrystalline SBN ceramics can be made with a larger size and more complex shape. Since, microstructure of the alkali-earth metal niobates affects critically the optical properties, the synthesis of SBN ceramic powders with good sinterability and compositional homogeneity is necessary. Traditional solid state method leads to poor compositional homogeneity and high sintering temperatures.

The properties of ceramics are greatly influenced by the characteristics of the powder such as particle size, morphology, purity and chemical composition. Wet chemical synthesis of ultrafine ceramic powders continues to be a subject of intense research activity as the products exhibit several advantages over powder derived from conventional ceramic routes. Using chemical methods, e.g. coprecipitation, sol–gel, hydrothermal and colloid emulsion technique, it has been confirmed to efficiently control the morphology and chemical composition of prepared powder. The main advantages of these methods are the increased homogeneity and high surface area of the resulting powders, which lead to relatively high reactivity and hence low sintering temperatures. Here we give a simple coprecipitation procedure to prepare $Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN) ceramics at low temperatures. Coprecipitation is one of the more successful techniques for synthesizing ultrafine ceramic powders having narrow particle size distribution (Dhage *et al* 2003). This process can avoid complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The only drawback of coprecipitation process is that the required cations should have similar solubility product.

2. Experimental

For preparing SBN ceramics, niobium (V) oxide, strontium chloride and barium chloride were used as starting materials, which were of AR grade (Loba chemie). Nb_2O_5 was dissolved in minimum amount of HF after heating in hot water bath for 10 h. To this NbF_5 solution, required quantity of $BaCl_2{\cdot}2H_2O$ and $SrCl_2{\cdot}2H_2O$ were added and mixed well. An excess quantity of concentrated HCl was added to the above solution to dissolve the barium (or strontium) fluoride formed by the mixing of NbF_5 and $BaCl_2{\cdot}6H_2O$ (or $SrCl_2{\cdot}6H_2O$). A mixture of ammonium oxalate and ammonium hydroxide was added dropwise to precipitate niobium and barium (and strontium) as hydroxides and oxalate, respectively. The pH was maintained at around 10 to ensure completion of the reaction. Then, the precursor powder precipitated was filtered and oven dried. The dried powders were calcined at different temperatures

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ranging from 400–1000°C for 6 h. Various techniques such as XRD (Philips PW 1710 Diffractometer) and TEM were employed to characterize these powders. For lattice parameter and interplanar distance (d) calculation, the samples were scanned in the $2q$ range of 10–80° for a period of 5 s in the step scan mode. Silicon was used as an internal standard. Least squares method was employed to determine the lattice parameters. The TEM picture was recorded with JEOL model 1200 EX instrument at the accelerating voltage of 100 kV. The fine powders were dispersed in amyl acetate on a carbon coated TEM copper grid. For comparison, SBN samples were also prepared by ceramic method. The corresponding oxides or carbonates were taken in stoichiometric ratio and mixed, ground several times and heated at 1000°C for 72 h. The calcined powders (from both precursor derived and ceramic method) were mixed with few drops of 1 wt% solution of poly vinyl alcohol and pelletized at 1–2 tons. The green pellets were sintered at 1300°C for 2 h. The surfaces of the sintered pellet were polished and electroded with low-temperature curing silver paint. The ferroelectric hysteresis loop parameters were measured with the aid of a home-built Sawyer-Tower circuit. A LCR meter was used to measure the dielectric constant at 1 kHz.

3. Results and discussion

Figure 1 shows the XRD pattern of SBN precipitate powder heated at 750°C. The crystal structure of SBN is tetragonal and all the d-spacings match with the reported values (JCPDS: 22–93). The calculated lattice parameters by least square fit are $a = 12{\cdot}387$ Å and $c = 3{\cdot}934$ Å. This is the lowest temperature reported so far for the formation of SBN by coprecipitation technique. Conventional solid state method also forms SBN phase at 1000°C after prolonged heating (72 h) with comparatively larger particle size of ~1 μm. The particle size and morphology of the calcined powders were examined by transmission electron microscopy. Particle morphology of calcined powder (750°C for 6 h) prepared by this technique was irregular in shape and agglomerated, with an average primary particle size of around 80 nm (figure 2). The particle size calculated from Scherrer's formula

$$t = Kl/B\cos q_B,$$

where t is the average size of the particles, assuming particles are spherical, $K = 0{\cdot}9$, l the wavelength of X-ray radiation, B the full width at half maximum of the diffracted peak and q_B the angle of diffraction, is 100 nm. The densities of all the sintered samples are above 92% of the single crystal values.

The ferroelectric hysteresis loop parameters for the present sample sintered at 1300°C showed the values of remnant polarization, $P_r = 1{\cdot}5$ μC/cm^2 and coercive field,

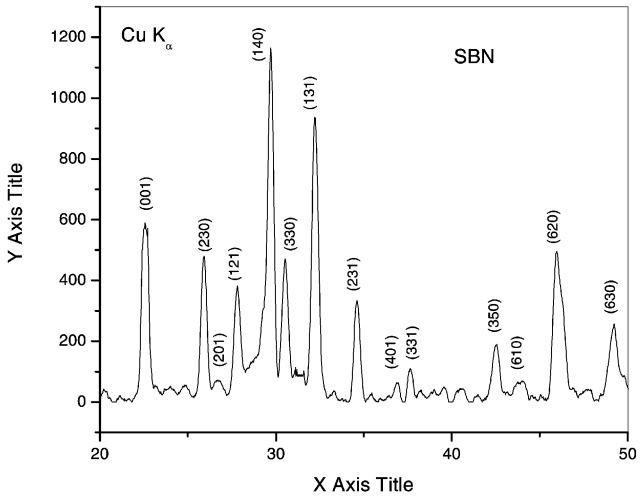

Figure 1. XRD of SBN powders after calcination at 750°C.

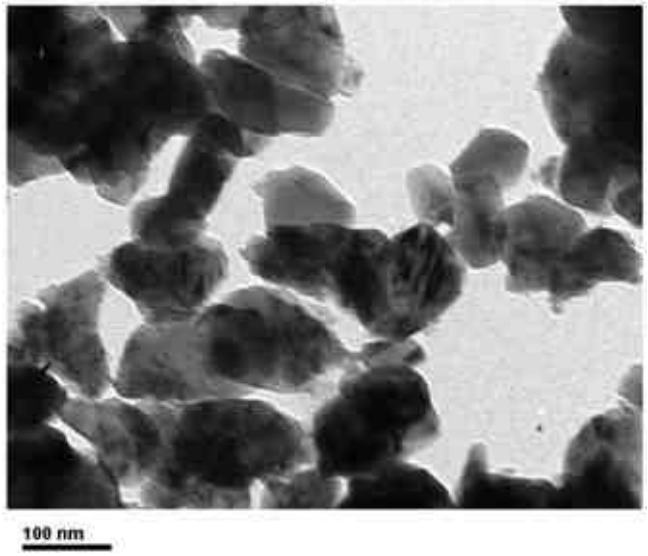

Figure 2. TEM micrograph of SBN powders calcined at 750°C.

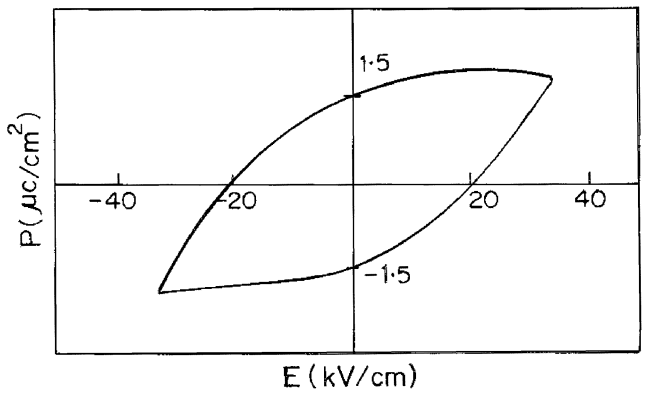

Figure 3. P–E loop for SBN ceramics (prepared by coprecipitation).

E_c = 20·5 kV/cm at an applied voltage of 60 kV/cm without any electric breakdown of the sample. The reported values of these parameters vary as E_c ~ 10–120 kV/cm and P_r ~ 6–10 μC/cm^2 depending on preparative conditions (Dhage *et al* 2005; Pasricha and Ravi 2005). It is well known that the ferroelectric properties obtained depends on sinter-density, grain size and defects present in the sample. The samples prepared by the ceramic technique have remnant polarization, P_s = 0·6 μC/cm^2 and coercive field, E_c ~ 10 kV/cm, at an applied field of 45 kV/cm without any electric breakdown. The room temperature relative dielectric constant measured at 1 kHz is 1100 for these samples.

4. Conclusions

A simple coprecipitation process is adopted for the preparation of ultrafine powders of SBN. The dielectric and ferroelectric properties of the SBN prepared by this process are also reported.

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